

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 07-090179

(43)Date of publication of application : 04.04.1995

(51)Int.Cl.

C08L 79/00

C08J 5/00

C08L 79/08

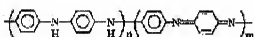
(21)Application number : 05-256316

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(22)Date of filing : 21.09.1993

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(54) COMPOSITE MOLDING AND ITS PRODUCTION



(57)Abstract:

PURPOSE: To obtain a polyaniline/polyimide composite molding excellent in heat resistance, strengths, etc., by heat-treating a molding of a polyaniline/ polyamic acid complex salt type precursor comprising a specified polyaniline and a specified polamic acid.

CONSTITUTION: A molding of a polyaniline/polyamic acid complex salt-type precursor comprising a polyaniline comprising structural units of formula I (wherein m and n are each 0 or greater; $m/(n+m)=0-1$; and $m+n=10-5000$) and having a number-average molecular weight of 2000-500000 and a polyamic acid represented by formula II (wherein Ar1 is a tetravalent aromatic-ring- containing group; Ar2 is a bivalent aromatic-ring-containing group; and k is 5-500) and having a number-average molecular weight of 1000-50000 is heat- treated to obtain a polyaniline/polyimide composite

molding comprising a polyaniline of formula I and a polyimide of formula III. When doped with an acceptor dopant, this molding can show a dielectric constant as high as about 10-3 to 10S/cm.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention is excellent in heat resistance and solvent resistance, and relates to a poly aniline polyimide composite molding body which has mechanical strength even with after [sufficient] doping, and a manufacturing method for the same.

[0002]

[Description of the Prior Art]Poly aniline as a new electronic industry material and an electrical conducting material in recent years. For example, the application to a wide range of fields, such as functional devices, such as the electrode material of a cell, a spray for preventing static electricity, an electromagnetic wave cutoff material, a photoelectron sensing element, optoelectronic memory, and a various sensor, a display device, various hybrid materials, a transparent electric conductor, and various terminal groups, is considered. However, since pi conjugated system is [poly aniline] generally highly developed, Since many firm hydrogen bonds exist between chains strongly [a polymers main chain is upright and / the interaction between chains], and it is insoluble to almost all organic solvents and does not fuse with heating, either, it has the big fault that processing of film-izing etc. is not deficiently made to a moldability. Therefore, for example, impregnate the substrate of the shape of a request of the textiles of a polymer material, a porous body, etc. with a monomer, and this monomer by contact with a suitable polymerization catalyst. Or it was made to polymerize by electrolytic oxidation, and under existence of thermoplastic polymer powder, it is considered as the charge of conductive composite, or the monomer was polymerized, and the same composite material has been obtained again. On the other hand, compounding poly aniline meltable only to N-methyl-2-pyrrolidone by the device of a polymerization catalyst and reaction temperature is also proposed (M. Abe et al.:J.Chem.Soc., Chem.Comm., 1989, 1736). However, this poly aniline hardly melts into other general-purpose organic solvents, either, but the adaptation range is restricted. If this meltable poly aniline is gelled in N-methyl-2-pyrrolidone and this is fabricated, a very tough film will be obtained, but becoming weak by a dope is known (O. Oka et al.Synth.Met.55-57 (1993) 999 - 1004). The poly aniline solubilized to the general-purpose solvent using organic sulfonic acid, Although it is reported that blending with general purpose grade polymer is also possible (A. J.Heeger et al.:Synth.Met.48(1992)91-97), Character which poly aniline has, such as heat resistance, toughness, and solvent resistance, will be governed by the blended general purpose grade polymer (namely, polymer of a matrix), and cannot be satisfied.

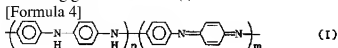
[0003]

[Problem(s) to be Solved by the Invention]This invention is made in view of the above actual condition in a Prior art. That is, the purpose of this invention is excellent in heat resistance and solvent resistance, and there is after doping in providing a poly aniline

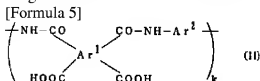
polyimide composite molding body which has sufficient mechanical strength, and a manufacturing method for the same.

[0004]

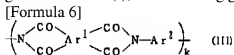
[Means for Solving the Problem]this invention person by forming a processible complex salt precursor and fabricating it, if poly aniline and polyamide acid are mixed as a result of inquiring wholeheartedly that the above-mentioned problem should be solved, It excelled in heat resistance and solvent resistance, and after doping found out that a poly aniline polyimide composite molding body which has sufficient mechanical strength was obtained. A poly aniline polyimide composite molding body of this invention is following general formula (I).



(type Naka, and m and n are zero or more integers, and are $m/(n+m)=0-1$ and $m+n=10-5000$. Poly aniline and following general formula (II) of the number average molecular weights 2000-500000 which consist of a structural unit which is) and is shown



(Ar¹ in a formula expresses the tetravalent basis which has an aromatic ring, and Ar² expresses the divalent basis which has an aromatic ring, and) k means the integer of 5-500. It is formed by heating the molded product of the poly aniline polyamide acid complex salt type precursor which consists of polyamide acid of the number average molecular weights 1000-500000 shown, Poly aniline shown by the above-mentioned general formula (I), and following general formula (III)



(Ar¹ in a formula, Ar², and k have the above and the meaning.) -- it consists of polyimide shown

[0005]The above-mentioned poly aniline polyimide composite molding body of this invention, Poly aniline of the number average molecular weights 2000-500000 which consist of a structural unit shown by the above-mentioned general formula (I). After fabricating the poly aniline polyamide acid complex salt type precursor obtained by mixing the polyamide acid of the number average molecular weights 1000-500000 shown by the above-mentioned general formula (II) in desired shape, therefore, it can manufacture to heat and make polyimide structure form. In this case, it is preferred to mix so that the carboxyl group of the polyamide acid shown by the above-mentioned general formula (II) may be 25-300-mol% to the nitrogen atom of the poly aniline which consists of a structural unit shown by the above-mentioned general formula (I).

[0006]If meltable to N-methyl-2-pyrrolidone, poly aniline used here, Although manufactured by what kind of method, oxidative polymerization of the aniline is carried out by using ammonium persulfate etc. as an oxidizer at temperature of low temperature,

for example, the range of -20-50 **, and meltable type poly aniline obtained by processing this aniline oxidation polymer with an ammonia solution is used suitably. In meltable type poly aniline obtained, although it is meltable to amide series solvents, such as N-methyl-2-pyrrolidone (NMP) and N,N-dimethylacetamide (DMAc), it is almost insoluble to other general-purpose organic solvents, for example, chloroform, and tetrahydrofurans.

[0007]In this invention, this meltable type poly aniline needs the number average molecular weights 2000-500000 and to have number average molecular weight of measurement and polystyrene conversion preferably at 5000-250000[GPC (N-methyl-2-pyrrolidone solvent). If a number average molecular weight of poly aniline becomes lower than 2000, the flexibility of a poly aniline polyamide acid complex salt type precursor and a poly aniline polyimide complex obtained eventually will be spoiled, and it will become difficult to obtain a self-standing film, a fiber, and other molded products. When 500000 is exceeded, solubility over a solvent becomes low and becomes on the other hand, less preferred in respect of preparation of a poly aniline polyamide acid complex salt type precursor or processing.

[0008]Polyamide acid shown by the above-mentioned general formula (II) is known as a precursor of the fusibility of polyimide, and the synthesizing method is also known well. In this invention, if a stage of formation of poly aniline and a complex salt type precursor is taken into consideration, a method of making tetracarboxylic dianhydride and diamine react to a synthesizing method of polyamide acid in NMP or DMAc is preferred. If this method is used, a poly aniline polyamide acid complex salt type precursor can be directly prepared in a reaction solution of polyamide acid, and separation and refining of polyamide acid can be excluded. A reaction of tetracarboxylic dianhydride and diamine dissolves one of compounds in an amide series solvent of NMP or the DMAc middle class, and it is performed by returning to a room temperature gradually, adding and stirring one of other compounds at about -20-0 ** low temperature. Although reaction time may reach more than 2 to 48 hours, or it, since it changes with combination of a starting material, it is suitably determined according to it. Reaction temperature can be arbitrarily chosen in room temperature -150 ** with combination of a starting material. Since a ring closure reaction of an imide ring may occur, it is not preferred that reaction temperature exceeds 150 **.

[0009]As tetracarboxylic dianhydride for forming the above-mentioned polyamide acid, Pyromellitic dianhydride, benzophenone tetracarboxylic dianhydride, What has aromatic rings, such as naphthalene tetracarboxylic dianhydride, biphenyl tetracarboxylic dianhydride, terphenyl tetracarboxylic dianhydride, diphenylsulfone tetracarboxylic dianhydride, an oxydi phthalic acid anhydride, and methylenebis (phthalic acid anhydride), is used. These tetracarboxylic dianhydride may be replaced by halogen atoms, such as alkoxy groups, such as alkyl groups, such as a methyl group, an ethyl group, and a propyl group, a methoxy group, an ethoxy basis, and a propoxy group, fluoride, chlorine, bromine, and an iodine.

[0010]On the other hand as diamine, a phenylenediamine, diaminobiphenyl, What has aromatic rings, such as oxydi aniline, methylenebis (aniline), bis(aminophenoxy)benzene, bis(aminophenoxy)biphenyl, and bis[(aminophenoxy) phenyl] propane, is used. These diamine may be replaced by halogen atoms, such as alkoxy groups, such as alkyl groups, such as a methyl group, an ethyl group, and a propyl group, a methoxy group, an ethoxy

basis, and a propoxy group, fluoride, chlorine, bromine, and an iodine. as the polyamide acid produced by performing it above in this invention -- the number average molecular weights 1000-500000 -- a thing of the range of 2000-250000 is used preferably.

[0011]In this invention, a poly aniline polyamide acid complex salt type precursor, In NMP or a DMAc solution of polyamide acid shown by general formula (II) produced by performing it above. It can form by stirring meltable type poly aniline which consists of a structural unit shown by the above-mentioned general formula (I) at a room temperature [solvent / same], and forming complex salt of amine and carboxylic acid. Formation of this complex salt advances only by carrying out mixed stirring of both. With formation of complex salt, the color of a solution can change from deep blue to deep green, and advance of complexing can check it by viewing. If formation of complex salt is not fully performed, an uneven complex will be formed, a fault is produced to flexibility or tough nature, and it becomes impossible to satisfy the purpose of this invention.

[0012]In this invention, the mixing ratio of poly aniline and polyamide acid becomes the mixing ratio of poly aniline in a composite molding body obtained eventually, and polyimide. Therefore, although what is necessary is just to mix both with the mixture ratio in a composite molding body obtained eventually fundamentally, In order to obtain plastic deformation possibility of, i.e., a processible poly aniline polyamide acid complex salt type precursor, it is preferred to mix to a nitrogen atom of the above-mentioned poly aniline, so that a carboxyl group of the above-mentioned polyamide acid may be 25-300-mol%. On the other hand, as for a weight ratio of character of bulk to the above-mentioned poly aniline, and the above-mentioned polyamide acid, it is preferred that it is in the range of 1:0.1-1:10.

[0013]A poly aniline polyamide acid complex salt type precursor in which plastic deformation is possible can be obtained from a complex salt solution produced by mixing as mentioned above by removing a solvent at low temperature. As for especially temperature at the time of removing a solvent, 150 ** or less is preferred 200 ** or less. When temperature becomes higher than 200 **, imide-ization of polyamide acid which forms poly aniline and complex salt advances, and it becomes impossible to obtain a poly aniline polyamide acid complex salt type precursor in which plastic deformation is possible. As a method of performing solvent removal at low temperature, a method of volatilizing a solvent at around 100 ** low temperature is also employable by ventilating inactive gas, such as desiccation under decompression, dry air, and nitrogen gas, for example.

[0014]at ordinary temperature, since plastic deformation was possible for a poly aniline polyamide acid complex salt type precursor produced by performing it above, rolled it to a sheet shaped, spinning was carried out to the shape of a fiber, and it was inserted in a mold -- it carries out and a fabricating operation is carried out to desired shape. A molded product of a poly aniline polyamide acid complex salt type precursor produced by carrying out a fabricating operation to desired shape ranks second, and carries out the ring closure of the polyamide acid by heating. Heating does not have 1 hour, what is necessary is just to perform it at temperature of not less than 200 ** in deactivating group bodies in a vacuum, such as argon and nitrogen, for 10 hours, and a polyamide acid portion in complex salt causes a ring closure reaction by it, Polyimide structure is formed and a poly aniline polyimide composite molding body which consists of poly aniline which consists of a structural unit shown by the above-mentioned general formula (I),

and polyimide shown by the above-mentioned general formula (III) is obtained.

[0015] If a poly aniline polyimide composite molding body of this invention obtained by the above method is among nitrogen, weight loss will hardly be accepted also at 400 °C or temperature beyond it. It has the outstanding physical properties that intensity in the case of film state hardly changes as compared with a case of a film of corresponding polyimide, either.

[0016] A poly aniline polyimide composite molding body of this invention shows about $[10^{-3} - 10 \text{ S/cm}]$ high conductivity by doping with an acceptor nature dopant. Anythings can be used for it, if a dopant in particular that can be used is not restricted and is used as a dopant when doping a poly aniline system conductive polymer. When an example is given, halogenated compounds, such as iodine, bromine, chlorine, and iodine trichloride, Various salts of proton acid, such as sulfuric acid, chloride, nitric acid, perchloric acid, and fluoroboric acid, and said proton acid, Aluminum trichloride, trichloride iron, a molybdenum chloride, an antimony chloride, Lewis acid, such as arsenic pentafluoride, acetic acid, trifluoroacetic acid, benzenesulfonic acid, Various kinds of compounds, such as polymer acid, such as organic acid, such as p-toluenesulfonic acid, dodecylbenzenesulfonic acid, and camphor sulfonic acid, polyethylene sulfonic acid, polyethylene carboxylic acid, polyacrylic acid, and polystyrene sulfonate, can be raised. About a method of making these compounds doping, there is no restriction in particular and all publicly known methods can be adopted. Generally, what is necessary is just to be able to contact the above-mentioned poly aniline polyimide composite molding body to a dopant compound, and it can be processed in the gaseous phase or the liquid phase. A method of doping electrochemically can also be used in the above-mentioned proton acid or a solution of the salt.

[0017]

[Example] Hereafter, an example explains this invention.

4.1 g of example 1 aniline and 21.9 g of concentrated hydrochloric acid were dissolved in water to have made 100 ml, and it cooled at -5 °C. 21.9 g of concentrated hydrochloric acid and ammonium persulfate 6.28g were dissolved in water to have made 100 ml, and it cooled at -10 °C, and this solution was also slowly dropped into the previous aniline solution, and continued stirring at -10 °C for 6 hours. After filtering the generated solid and fully washing with water, a 1 more-N ammonia solution performed dedope processing for 10 hours. Fully drying this, the number average molecular weight obtained poly aniline of 12000 (it is a number average molecular weight of measurement and polystyrene conversion in GPC and NMP). This was used as manufacturing raw materials of the composite molding body indicated below. Next, the pyromellitic dianhydride of equimolar was added slowly, having dissolved 0.05 mol of bis(4-aminophenyl)ether in 160 g of refined N,N-dimethylacetamide (DMAc), having cooled at 0 °C, and stirring violently. Furthermore DMAc 30g was added, stirring was continued at the room temperature for 1 hour, and the DMAc solution of consistency polyamide acid was obtained. The number average molecular weight of this polyamide acid was 10000 (degree-of-polymerization $k =$ about 25) by GPC. The 2.5 % of the weight of DMAc(s) solution 17g of the poly aniline compounded previously was added to the DMAc solution 10g of this polyamide acid, and it stirred well (the carboxyl group of polyamide acid is 100-mol % to the nitrogen atom of poly aniline). By [with a deep color of the solution of poly aniline of the mixed beginning] continuing stirring, although it was blue, it changed

to dark green and it was checked that the complex salt of poly aniline and polyamide acid had been formed. After stirring for 2 hours, the obtained solution was cast on the glass substrate, it dried in 100 °C for 4 hours under the nitrogen air current, and the poly aniline polyamide acid complex salt precursor film in which plastic deformation is possible was obtained. Although this film could change variously, extended twice for measurement of conductivity or a mechanical strength, fixed with the shape of a film, performed heat-treatment in 250 °C for 2 hours under the vacuum, the ring closure reaction was made to cause, and the poly aniline polyimide complex film made into the purpose was obtained. When the infrared absorption spectrum before and behind heat-treatment was measured, the absorption near 1650-cm^{-1} of the amide origin which existed before heat-treatment disappeared, and it was checked that the absorption band which newly originates in imide 1720 and near 1780-cm^{-1} had appeared. It dried, after being immersed in a 2-N hydrochloric acid aqueous solution for 2 hours and washing the surface by aqua destillata lightly, in order to give conductivity to the complex film produced by performing it above. The conductivity was measured. A result is shown in the after-mentioned table 1.

[0018] In example 2 Example 1, the diamine component used as a raw material of polyamide acid, Replace with a methylenebis anisidine and a number average molecular weight creates the polyamide acid of 9000 (k = about 20). The poly aniline polyimide complex film was obtained by the completely same operation as Example 1 except mixing to nitrogen of poly aniline, so that the carboxyl group of polyamide acid may be 93-mol%. About this complex film, dope processing was performed like Example 1.

In example 3 Example 1, the diamine component used as a raw material of polyamide acid, Replace with bis[(aminophenoxy) phenyl] propane and a number average molecular weight creates the polyamide acid of 12000 (k = about 20). The poly aniline polyimide complex film was obtained by the completely same operation as Example 1 except mixing to nitrogen of poly aniline, so that the carboxyl group of polyamide acid may be 97-mol%. About this complex film, dope processing was performed like Example 1.

In example 4 Example 1, the diamine component used as a raw material of polyamide acid, Replace with m-FENIRENN diamine and a number average molecular weight creates the polyamide acid of 15000 (k = about 49). The poly aniline polyimide complex film was obtained by the completely same operation as Example 1 except mixing to nitrogen of poly aniline, so that the carboxyl group of polyamide acid may be 105-mol%. About this complex film, dope processing was performed like Example 1.

[0019] In example 5 Example 1, the tetracarboxylic dianhydride ingredient used as a raw material of polyamide acid is replaced with benzophenone tetracarboxylic dianhydride, The number average molecular weight created the polyamide acid of 9000 (k = about 19), and obtained the poly aniline polyimide complex film by the completely same operation as Example 1 except mixing to nitrogen of poly aniline, so that the carboxyl group of polyamide acid may be 93-mol%. About this complex film, dope processing was performed like Example 1.

In example 6 Example 1, the tetracarboxylic dianhydride ingredient used as a raw material of polyamide acid is replaced with methylenebis (phthalic acid anhydride). The number average molecular weight created the polyamide acid of 10900 (k = about 22), and obtained the poly aniline polyimide complex film by the completely same operation as Example 1 except mixing to nitrogen of poly aniline, so that the carboxyl group of polyamide acid may be 100-mol%. About this complex film, dope processing was

performed like Example 1.

[0020] Those characteristics were investigated about the poly aniline polyimide complex film given in the above-mentioned Examples 1-6, and the film obtained from poly aniline. The result is shown in the following table 1.

[Table 1]

	弾性率 (GPa)	引張強度 (MPa)	分解開始温度 (℃)	導電率 (S cm ⁻¹)
ポリアニリン	1.3/1.5	52/39	400/250	<10 ⁻¹⁰ /25
実施例 1	100/110	540/520	350/350	<10 ⁻¹⁰ /1.5
実施例 2	110/115	450/400	300/270	<10 ⁻¹⁰ /2.5
実施例 3	105/110	450/410	320/290	<10 ⁻¹⁰ /0.5
実施例 4	250/260	600/600	400/390	<10 ⁻¹⁰ /0.2
実施例 5	120/150	430/390	350/300	<10 ⁻¹⁰ /0.1
実施例 6	100/105	450/400	350/350	<10 ⁻¹⁰ /0.1

注) ドープ前/ドープ後

The poly aniline polyimide complex film of each example has a mechanical property superior to a poly aniline independent thing, and dope processing also showed that there was almost no strong fall so that clearly from the result of Table 1.

[0021]

[Effect of the Invention] The poly aniline polyimide composite molding body of this invention can be excellent in heat resistance and a mechanical strength, can show high conductivity by dope processing, and can use it for various uses as an electronic industry material and an electrical conducting material. The Plastic solid of desired shape can be easily created by the method of this invention about the poly aniline polyimide complex for which creation of the Plastic solid was conventionally difficult.

[Translation done.]